

1/1

(12) **UK Patent Application** (19) **GB** (11) **2 164 785 A**

(43) Application published 26 Mar 1986

(21) Application No 8522162

(22) Date of filing 6 Sep 1985

(30) Priority data

(31) 8422546
8507185

(32) 6 Sep 1984
20 Mar 1985

(33) GB

(51) INT CL⁴

H01M 4/90

(52) Domestic classification

H1B F102 F10 F202 F204 F206

(56) Documents cited

GB A 2108312
GB 1213364

GB 1207392

EP 0107612

(58) Field of search

H1B
C7B

(71) Applicant

National Research Development Corporation (United Kingdom),
101 Newington Causeway, London SE1 6BU

(72) Inventors

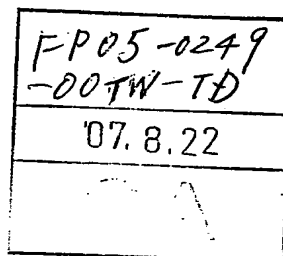
John Bannister Goodenough
Ashok Kumar Shukla
Carlos Antonio Da Silva Paliteiro
Keith Roderick Jamieson
Andrew Hamnett
Ramasamy Manoharan

(74) Agent and/or Address for Service

P W Neville,
Patents Department, National Research Development Corporation, 101 Newington Causeway, London SE1 6BU

(54) Electrode for reducing oxygen

(57) An electrode for reducing oxygen has a substrate of low-ash carbon, such as coconut shells converted to charcoal. The substrate is loaded with a catalyst such as (i) platinum phthalocyanine or (ii) lead-ruthenium oxide. In case (ii), to make the electrode, lead ions are adsorbed onto the substrate, which is then treated with a solution of ruthenium (VI) oxide, to precipitate the catalyst on the substrate. Macrocyclic derivatives of transition metals or of Cu, Ag, Au, Zn, Cd, Hg, In, Tl, Sn, Pb, Sb or Bi may be used as the catalyst and the electrode may be employed in fuel cells.



SPECIFICATION

Electrode for reducing oxygen

- 5 This invention relates to an electrode for reducing oxygen, to a fuel cell including such an electrode, to a method of reducing oxygen at such an electrode, and to a method of making certain such electrodes.
- 10 According to the present invention, an electrode for reducing oxygen comprises a substrate which is an electronic conductor capable of reducing elemental oxygen to water yielding not more than 5% (preferably not more than 1%, more preferably not more than 0.1%) hydrogen peroxide, to which substrate is attached a catalyst which can reduce elemental oxygen to water yielding not more than 5%, (preferably not more than 1%, more preferably not more than 0.1%) hydrogen peroxide when used at cathodic potentials of -300 mV against the Hg/HgO electrode in alkaline or non-alkaline solution.

- A preferred suitable substrate is carbon of an ash content less than 0.1%, preferably less than 0.05%, preferably not more than 0.01%. An example of such a carbon is 'coconut carbon', which is derived from coconut shells by converting these to charcoal, washing and comminuting the charcoal, and exposing the comminuted charcoal to gas, preferably first carbon dioxide and, preferably, afterwards, ammonia. Another example is carbon which is of amorphous type and has a surface area of at least 200 m²/g, a mean particle size in the range 5 nm to 50 nm, and an apparent density of 80 to 110 kg/m³, which may be treated by comminuting it and exposing it to gas at elevated temperature. Preferably the carbon before the treatment has a surface area of not more than 300 m²/g. Preferably the carbon before the treatment has a pH below 7. The carbon may be exposed to only carbon dioxide, for example at 800°C to 1000°C, preferably for 40 to 90 minutes, such as 900°C for 1 hour.

Preferred suitable catalysts are:

- (i) macrocyclic derivatives of transition metals or of B-metals (i.e. Cu, Ag, Au, Zn, Cd, Hg, In, Tl, Sn, Pb, Sb or Bi) for example platinum phthalocyanine, and
- (ii) oxides containing ruthenium, for example $Pb_{2-x}Ru_xO_{6+y}$, where $0 \leq x \leq 1$ or $Pb_{2-x}Bi_yRu_xO_{6+y}$, where x is from 0 to 2 and y is from 0 to 1.
- 55 Catalyst loadings in case (i) are 1 to 15% by weight of the substrate, preferably 2 to 12%.

- Hitherto, efforts in the art of reducing oxygen at an electrode have been directed mainly towards minimising or circumventing the harmful effects of hydrogen peroxide which is evolved at the electrode. It has not hitherto been attempted to select electrode materials on the basis of their low production of hydrogen peroxide, except for attempts to inhibit

hydrogen peroxide evolution by gold-plating carbon.

- The invention extends to a fuel cell including an electrode as set forth above. The invention also provides a method of reducing oxygen, comprising contacting elemental oxygen with a source of hydrogen (such as a hydroxide solution) at an electrode as set forth above and applying to the electrode a potential of from 0.1 to -0.2 volts with respect to the Hg/HgO electrode. For example, where the catalyst is platinum phthalocyanine with an electrolyte of 6M KOH, the potential is preferably from 0.1 to -0.2 V, and where the catalyst is lead ruthenate (nominally $Pb_{2-x}Ru_xO_{6+y}$) with an electrolyte of 1M KOH, the potential is preferably 0.2 to -0.2 V; at more positive potentials, no appreciable reduction current flows; at more negative potentials, currents become excessive. Alternatively, the source of hydrogen may be an acid or neutral aqueous solution.

- According to another aspect, the invention provides a method of making an electrode as set forth above, wherein the catalyst is an oxide containing ruthenium and another metal, comprising adsorbing ions of the other metal onto the substrate and treating the substrate with a solution of ruthenium oxo-anion complex (nominally ruthenium (VI) oxide), whereby the desired catalytic oxide is precipitated on, and is attached to, the substrate. The invention extends to the electrode so made, and to fuel cells, methods of reducing oxygen etc. using it. For use in alkaline media, the 'coconut' carbon is preferred, preferably with catalysts of case (ii) above. For use in acid media, the amorphous carbon is preferred, preferably with catalysts of case (i) above or e.g. thiocyanate.

The invention will now be described by way of example. In the accompanying drawings,

- Figures 1 and 2 show the performance of electrodes according to Examples 1 and 2 of the invention respectively, compared with other electrodes, under various conditions.

SUBSTRATE PREPARATION EXAMPLE

- A porous carbon electrode is made utilising coconut shell charcoal.

- Active coconut shell charcoal obtained from Talaulicar carbons (P) Ltd., Londa, India, was subjected to repeated gravity separation with saturated calcium chloride solution to remove any denser ingredients and then subjected to repeated 'Soxhlet' treatment with azeotropic hydrochloric acid and then repeatedly washed in the 'Soxhlet' itself with distilled water. After drying in a vacuum oven at 150°C, the ash content of this carbon was found to be about 0.03%. This charcoal was subjected to mechanical grinding and sieving through a 400 mesh sieve. This carbon was gas-activated by heating in a carbon-dioxide atmosphere at 900°C for 4 hours and then in an ammonia

atmosphere also at 900°C for 4 hours. Gas-activation was chosen instead of further grinding, to minimise agglomeration.

- Substrates for electrodes were prepared by
 5 hot (140°C) pressing, under 0.05 tonne cm⁻², this gas-activated carbon mixed with 20% by weight polyethylene powder (5 micron average particle size) onto an expanded platinum mesh (0.06 mm diameter wire, at 0.3 mm centres).
 10 The BET surface area of such a substrate was about 600 m²/g and the resistivity about 0.4 ohm cm.

- An electrochemical cell for measuring electrochemical performance parameters was set up containing this substrate as a working electrode, a Hg/HgO, OH⁻ reference electrode, a high surface area flatbed counter electrode, and an electrolyte, which was a 27% KOH solution in distilled water. The cell was operated with a current density of 100 mA/cm² on the working electrode at a potential of -0.125 V against the reference electrode at 30°C, and oxygen was reduced to water with minimal (under 1%) by-production of hydrogen peroxide.
 25

ELECTRODE EXAMPLE 1

- Porous carbon for an electrode substrate was made as described in the Substrate Preparation Example, up to and including the gas-activation but excluding the hot pressing. Platinum phthalocyanine was dissolved in the least possible quantity of concentrated sulphuric acid, and then the carbon was dispersed into the solution. The solution was then diluted slowly with the least quantity of distilled water to obtain a slurry. The slurry is stirred with the carbon for one hour, washed until the supernatant liquor has a pH of 5 to 7, and then centrifuged. The carbon is dried and hot-pressed at 0.05 tonne cm⁻² with polyethylene binder as in the Substrate Preparation Example.
 30
 35
 40

- In Fig. 1, the performance oxygen reduction of various electrodes is compared. In all cases, the electrolyte was 6M aqueous KOH under a pressure of gaseous oxygen of 130 mB, at 35°C. The performance of the electrode just described is curve 1A (5% platinum phthalocyanine) and curve 1B (10% platinum phthalocyanine).
 45
 50

- The other curves represent other electrodes:
 a=untreated carbon (=a of Fig. 2)
 b=a+7% platinum (=b of Fig. 2)
 55 c=carbon according to Substrate Preparation Example (=c of Fig. 2)
 d=c+7% platinum

- Curve 1A lies above the others at all current densities over 150 mA/cm², and 1B above the others over 400 mA/cm². Life-time tests on 1A and 1B showed high stability at current densities of up to 400 mA/cm².
 60

ELECTRODE EXAMPLE 2

- In this Example, a novel method is featured
 65

for attaching a catalyst to a substrate.

- A porous carbon substrate was made as described in the Substrate Preparation Example. The catalyst Pb₂₊Ru₂O_{6+x} was precipitated on the substrate by a surface chemical reaction between Pb²⁺ pre-adsorbed on the substrate and a ruthenium complex in solution. This was achieved as follows:
 70

- The substrate was dipped for 30 minutes in a 0.001M aqueous solution of lead nitrate Pb(NO₃)₂. In this way, lead ions Pb²⁺ were adsorbed on the surface of the substrate. Meanwhile, a ruthenium solution was made by fusing 0.1 g RuO₂, 0.5 g NaOH and 5 g KNO₃ for 5 minutes and diluting the melt with distilled water to 250 ml. The dipped substrate was then dipped for 30 minutes in this ruthenium solution, whereby the catalyst Pb₂₊Ru₂O_{6+x} was precipitated on, and bound to, the surface of the substrate. This reaction is rather sensitive to pH; the above quantities ensure a suitable pH.
 75
 80
 85

After dipping and rinsing in distilled water, the resulting electrode is dried at 70°C.

- In Fig. 2, the performance of various electrodes at reducing oxygen is compared. In each case except curve 2 the electrolyte was 6M aqueous KOH under pressure of gaseous oxygen of 160 mB, at 35°C. The performance of the electrode just described is curve 2, in which the electrolyte was 1M aqueous KOH under a pressure of gaseous oxygen of 160 mB, at 35°C.
 90
 95

- The other curves represent other electrodes:
 100 a=untreated carbon (=a of Fig. 1)
 b=a+7% platinum (=b of Fig. 1)
 c=carbon according to Substrate Preparation Example (=c of Fig. 1)
 d=proprietary treated carbon + 15% platinum.
 105

e=teflon (40%)-bonded untreated carbon. Although showing high activity, this sample is short-lived because it evolves hydrogen peroxide, which degrades it; electrodes c and d do not exhibit such evolution.
 110

f=pyrochlore on untreated carbon substrate.

SECOND SUBSTRATE PREPARATION EXAMPLE

- High-surface-area Vulcan XC-72 carbon was obtained from the Cabot Corp., Billerica, MA. The ash content of this carbon was found to be about 0.05%. The other physical and chemical parameters of this carbon are as follows:
 115
 120

Surface area	257 m ² /g
Mean particle size	30 nm
Approximate density	96 kg/m ³
125 pH	5

- This carbon was subjected to mechanical grinding and then gas-activated by heating in a CO₂ atmosphere at 900°C for 1 hour. Gas activation rather than continued grinding was
 130

chosen to minimise particle agglomeration; it produced a 27% weight loss of the carbon, increased the effective surface area, and modified the surface.

5 The desired quantity of platinum was dispersed into the gas-activated carbon by reducing chloroplatinic acid with sodium formate solution as described elsewhere. This procedure yields fine platinum particles of uniform size
10 (about 63Å diameter) on a carbon substrate. Chloroplatinic acid solution containing the required proportion of platinum was taken from a 2 weight % stock solution, mixed with half of its volume of isopropanol, and neutralised
15 with a dilute solution of sodium carbonate. An appropriate quantity of gas-activated Vulcan XC-72 carbon was added, and the entire mixture was dried in an air oven before it was added, with vigorous stirring, to an excess of
20 boiling 5 weight % sodium formate solution to reduce the chloroplatinic acid to platinum metal. The resulting mass was filtered and washed repeatedly with hot, distilled water before being dried in an air oven.

25 Teflon-bonded electrodes were prepared for electrochemical measurements under gas-fed conditions. The Teflon binder provides the necessary mechanical strength to prevent electrode collapse under the gas pressure required
30 for gas-electrolyte interface control in a gas-diffusion electrode, and it does so while retaining the necessary electrode porosity. The Teflon-bonded electrodes were made as follows: Tetrahydrofuran (THF) was added to a
35 measured quantity of catalysed substrate powder in a beaker, and the mixture was agitated in an ultrasonic bath for about 30 minutes before a few ml of dilute suspension of Teflon emulsion (ICI GP2 Fluon dispersion, particle
40 size 0.1–0.2 microns) was added to the mixture without interruption of the agitation. The product material was centrifuged repeatedly with THF and finally spread on a platinum expanded-metal (Exmet) screen (0.076 mm diameter wire, 1024 mesh cm⁻²). The coated
45 screen was air-dried for about 15 minutes before it was cold-pressed at 125 kg cm⁻² for 5 minutes. The pressed mass was dried for 2 hours at 110°C and then cured in air at 360°C
50 for 30 minutes. The Teflon content of the electrodes was optimal at 25 to 35% by volume.

Short-term polarisation curves were obtained for dioxygen reduction in 5M H₂SO₄ solution
55 on various Vulcan XC-72 carbon electrodes.

Polarisation curves were obtained at 20°C for unplatinised carbon electrodes that were not gas-activated. Although the electrodes function at current densities of 400 to 600
60 mA cm⁻², their polarisation values are high.

Further curves were obtained on gas-activated Vulcan XC-72 substrates impregnated with 7 weight % dispersed metal and loaded with 30% Teflon and clearly show a sufficiently reduced mass-transfer polarisation for
65

loading of the electrodes to high current densities. These electrodes could be loaded intermittently at current densities of 1.1 A cm⁻² for periods of several minutes. This enhanced
70 performance indicates that the high-temperature CO₂ treatment has not only increased the surface area, but has also produced a well defined pore structure that optimises a uniform gas diffusion into the electrode. It also
75 indicates a good platinum dispersion on the surface, and any surface modification by the CO₂ treatment would appear to be beneficial. No detectable H₂O₂ was evolved, whereby the carbon was not destroyed from this cause
80 (improving the lifetime of the electrode) and whereby efficiency was improved (none of the reduced oxygen being wastefully converted to reappear as H₂O₂).

To put the foregoing into context, the long-range goal of fuel-cell research is the development of fuel-cell batteries that operate on inexpensive fuels and have air as the oxidant. These batteries must convert chemical energy to electric power with high efficiency at practical current densities; they must also have long
90 operational life—or a low-cost replacement of ageing parts—if they are to compete with present forms of power generation from the same inexpensive fuels.

A primary impediment to the commercial realisation of fuel-cell technology is failure to identify suitably catalytic electrodes having a long operational life in acidic electrolytes. Alkaline electrolytes react with carbon dioxide to form carbonates that foul the electrodes. Although fouling by CO₂ from the air can be slowed to nearly tolerable rates for low-cost, exchangeable alkaline air electrodes in a pure hydrogen-air fuel cell, an acidic electrolyte has
105 great advantages.

High performance requires fabrication of a porous electrode substrate of high surface area on which a suitable catalyst is effectively disposed; moreover, the effective surface area must not be degraded by normal operational conditions. Degradation may be caused by:
110 (1) chemical attack from the product of an unwanted side reaction,
(2) porosity,
115 (3) mechanical collapse, or
(4) sintering due to heat from internal losses.

Therefore attention must be directed to the choice of substrate material and catalyst as well as to the method of electrode fabrication and catalyst dispersion.
120

Selection of a suitable substrate material is dictated by at least six factors: cost, inertness in operating medium, ease of fabrication in colloidal-size particles, high electrical conductivity, effectiveness as substrate for a highly dispersed catalyst, and inertness to unwanted side reactions. Various types of active (high-surface-area) carbon have been examined as supports for platinum-metal catalysts in elec-
130

trodes used for both oxygen reduction and methanol oxidation in acid solution. Carbons of low ash content prove to be superior; these appear to be free of the impurities responsible for hydrogen-peroxide generation, a side reaction responsible for chemical attack of the substrates. Vulcan XC-72 carbon, made by Cabot Corp., which has a low ash content, functions as an excellent air-electrode substrate in acid if its surface is suitably pre-treated and platinum is uniformly dispersed onto it. Such a Teflon-bonded electrode as set forth above appears to reduce dioxygen to water in 5M H₂SO₄, with no detectable formation of hydrogen peroxide and to be able to sustain load currents of about 900 mA cm² for long periods without serious degradation.

CLAIMS

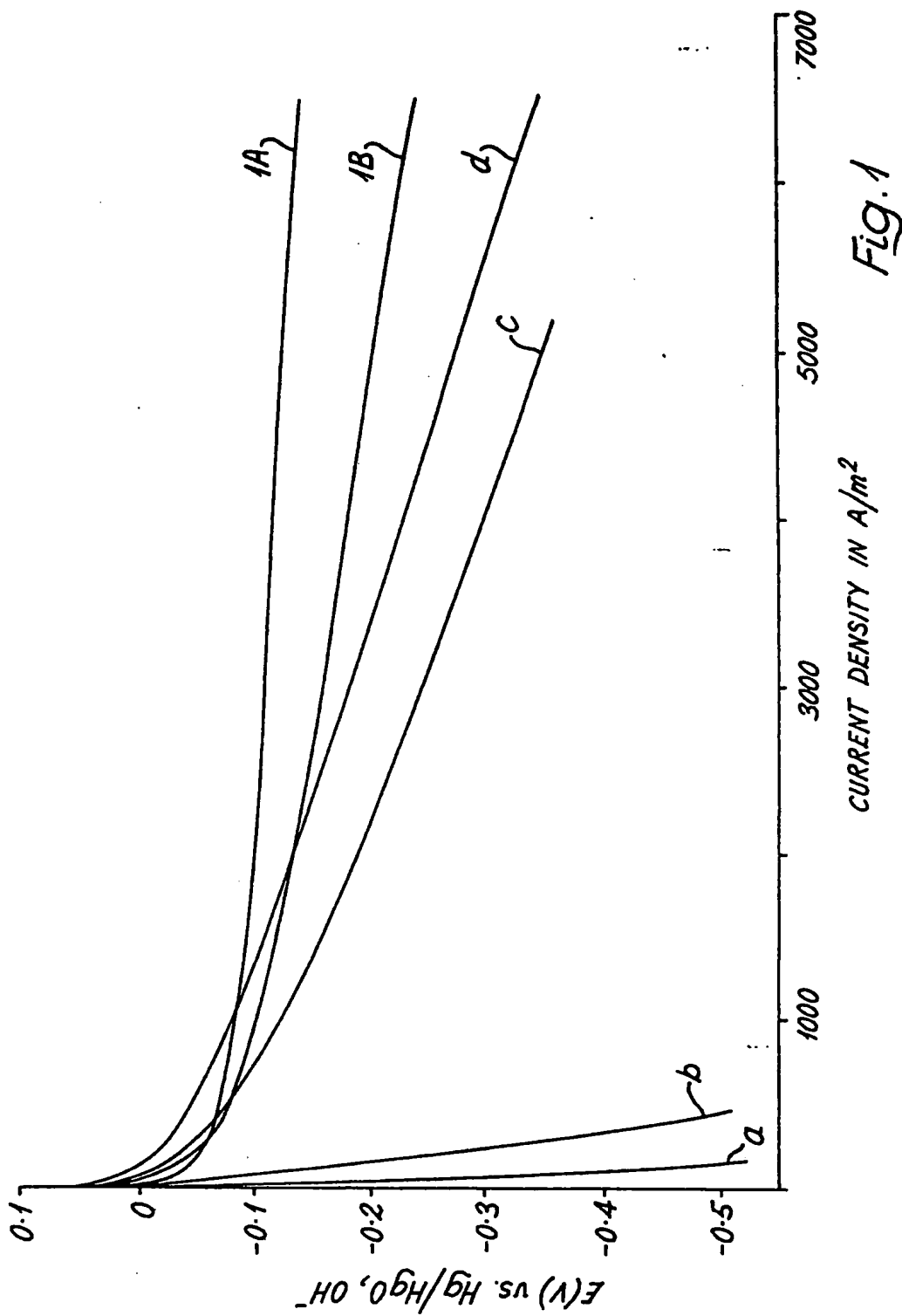
- 20 1. An electrode for reducing oxygen, comprising a substrate which is an electronic conductor capable of reducing elemental oxygen to water yielding not more than 5% hydrogen peroxide, to which substrate is attached a catalyst which can reduce elemental oxygen to water yielding not more than 5% hydrogen peroxide when used at cathodic potentials of -300 mV against the Hg/HgO electrode in alkaline or non-alkaline solution.
- 25 2. An electrode according to Claim 1, wherein the electronic conductor is capable of reducing elemental oxygen to water yielding not more than 1% hydrogen peroxide.
- 30 3. An electrode according to Claim 2, wherein the catalyst can reduce elemental oxygen to water yielding not more than 1% hydrogen peroxide.
- 35 4. An electrode according to Claim 3, wherein the electronic conductor is capable of reducing elemental oxygen to water yielding not more than 0.1% hydrogen peroxide.
- 40 5. An electrode according to Claim 4, wherein the catalyst can reduce elemental oxygen to water yielding not more than 0.1% hydrogen peroxide.
- 45 6. An electrode according to any preceding claim, wherein the substrate is carbon of an ash content less than 0.1%.
- 50 7. An electrode according to Claim 6, wherein the said ash content is less than 0.05%.
- 55 8. An electrode according to Claim 7, wherein the said ash content is less than 0.01%.
- 60 9. An electrode according to any preceding claim, wherein the carbon is 'coconut carbon'.
- 65 10. An electrode according to Claim 9, wherein the carbon is derived from coconut shells by converting these to charcoal, washing and comminuting the charcoal, and exposing the comminuted charcoal to gas.
11. An electrode according to Claim 10, wherein the gas is first carbon dioxide and afterwards ammonia.
12. An electrode according to any of Claims 1 to 8, wherein the substrate is made by treating the carbon, which is of amorphous type and has a surface area of at least 200 m²/g, a mean particle size in the range 5 nm to 50 nm, and an apparent density of 80 to 110 kg/m³, by comminuting it and exposing it to gas at elevated temperature.
13. An electrode according to Claim 12, wherein the carbon before the treatment has a surface area of not more than 300 m²/g.
14. An electrode according to Claim 12 or 13, wherein the carbon before the treatment has a pH below 7.
15. An electrode according to Claim 12, 13 or 14, wherein the gas to which the carbon is exposed is carbon dioxide.
16. An electrode according to Claim 15, wherein the said elevated temperature is from 800 C to 1000 C.
17. An electrode according to Claim 16, wherein the duration of the exposure at said elevated temperature is from 40 to 90 minutes.
18. An electrode according to any of Claims 12 to 17, when in use to reduce oxygen to water in an acid medium.
19. An electrode according to any of Claims 9 to 11, when in use to reduce oxygen to water in an alkaline medium.
20. An electrode according to any preceding claim, wherein the catalyst is a macrocyclic derivative of transition metals or of B-metals (i.e. Cu, Ag, Au, Zn, Cd, Hg, In, Tl, Sn, Pb, Sb or Bi).
21. An electrode according to Claim 20, wherein the catalyst loading is 1 to 15% by weight of the substrate.
22. An electrode according to Claim 21, wherein said catalyst loading is 2 to 12%.
23. An electrode according to any of Claims 1 to 19, wherein the catalyst is an oxide containing ruthenium.
24. An electrode according to Claim 23, wherein the catalyst is an oxide containing ruthenium and one or more other metals.
25. An electrode according to Claim 24, wherein the catalyst is Pb₂-Bi₂Ru₂O₈, where x is from 0 to 2 and y is from 0 to 1.
26. A method of making an electrode according to Claim 24 or 25, comprising adsorbing ions of the other metal(s) onto the substrate and treating the substrate with a solution of ruthenium oxo-anion complex, whereby the desired catalytic oxide is precipitated on, and is attached to, the substrate.
27. An electrode made by a method according to Claim 26.
28. A fuel cell including an electrode according to any of Claims 1 to 25 or 27.
29. A method of reducing oxygen, comprising contacting elemental oxygen with a source of hydrogen at an electrode according to any of Claims 1 to 25 or 27, and applying to the electrode a potential of from 0.1 to -0.2 volts with respect to the Hg/HgO elec-

trode.

30. A method according to Claim 29,
wherein the current density exceeds 8000
A/m².

Printed in the United Kingdom for
Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.

1/2



2/2

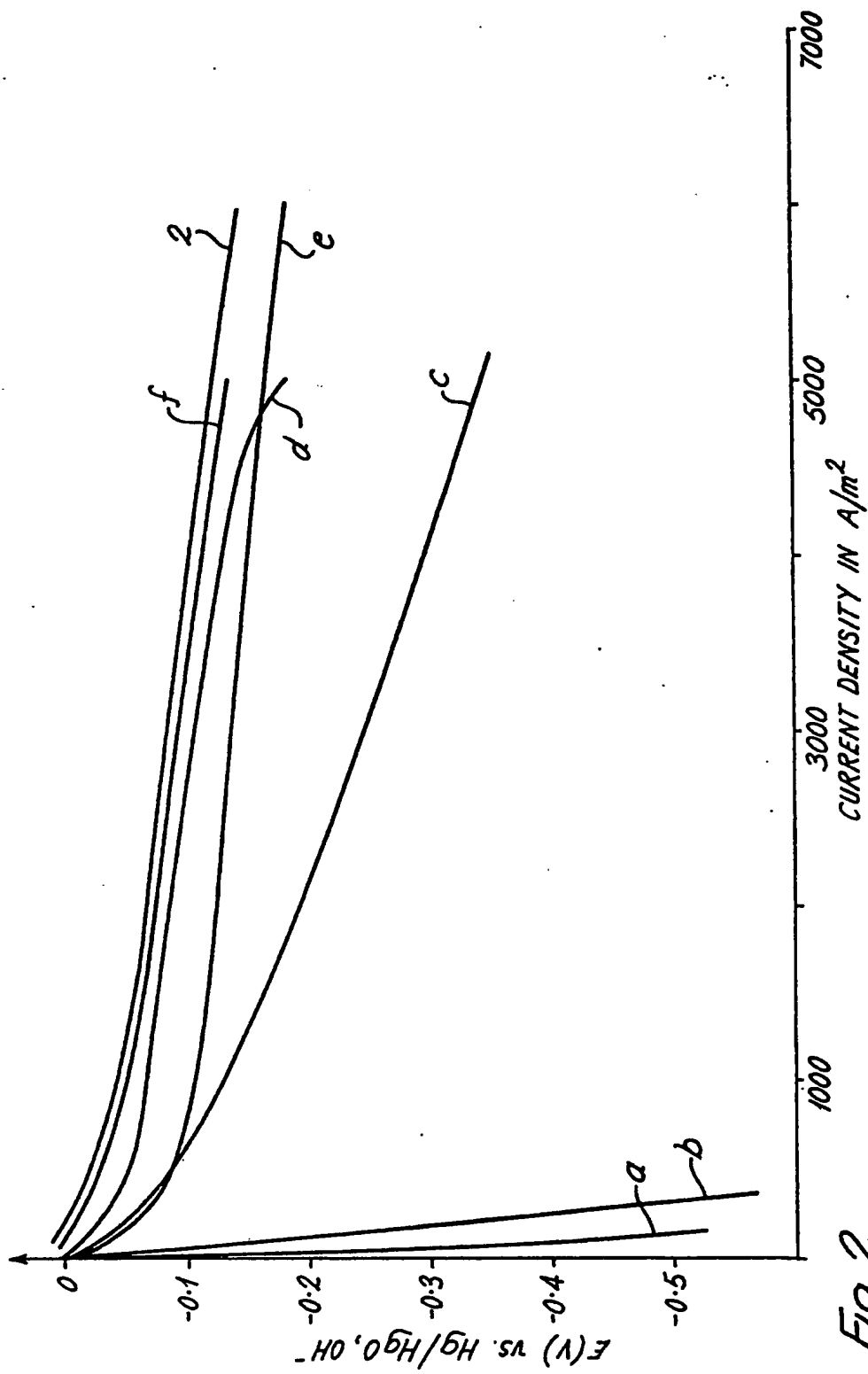


Fig. 2